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Chemical adsorption of liquid organochlorine compounds as a method of purification of pyrolytic oil

RAPID COMMUNICATION

Summary — In this work, a new method of purification of pyrolytic oil from organochlorine compounds with silver or platinum adsorbents was proposed and tested. The experiments carried out at temperatures from 20 up to 200 °C have shown that chosen for studies organochlorine compounds were well adsorbed from the prepared solutions. Eminently respectable results were found for silver adsorbent. A high initial cost of such adsorbents mandates their regeneration. It has been shown that it is possible to clear the adsorbent surface with hydrogen at the temperature 300—350 °C. A residue on the surface (after several cycles of adsorption/regeneration) can be burned with air.
Keywords: dechlorination of pyrolytic oil, chemical adsorption, silver, platinum, regeneration.

ADSORPCJA CHEMICZNA CIEKŁYCH ZWIĄZKÓW CHLOROORGANICZNYCH JAKO METODA OCZYSZCZANIA OLEJU PIROLITYCZNEGO
Streszczenie — W pracy przedstawiono wyniki wstępnych badań możliwości zastosowania metalicznego srebra oraz platyny (naniesionych na Al_2O_3) jako adsorbentów związków chloroorganicznych zanieczyszczających olej pirolityczny będący ciekłą mieszaniną węglowodorów (z przewagą węglowodorów alkiloaromatycznych). Eksperymenty wykonane w temp. 20—200 °C potwierdziły, że wybrane do badań związki chloru były dobrze adsorbowane z przygotowanych roztworów za pomocą srebra (tabela 1, rys. 1). Wykazano również, że zużyty adsorbent można zregenerować w temp. 300—350 °C za pomocą wodoru, a osad nawarstwiający się w trakcie wielokrotnego powtarzania cyklu adsorpcja/regeneracja adsorbentu można wypalić w tej samej temperaturze za pomocą powietrza (rys. 2).
Słowa kluczowe: odchlorowanie oleju pirolitycznego, adsorpcja chemiczna, srebro, platyna, regeneracja.

It is estimated that municipal plastic waste (MPW) contains polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC), poly(ethyl terephthalate) (PET) and acrylonitrile-butadiene-styrene copolymer (ABS) [1]. The content of other plastics is negligible from the point of view of most studies. In the pyrolytic oils obtained from mixtures of PVC with polyolefins some organochlorine compounds can be detected — among which 2-chloro-2-methylpropane, 2-chloro-2-phenylpropane and (α-chloroethyl) benzene have been identified [2—4]. Many more organochlorine compounds have been identified in the oils derived from mixtures of PVC with PET and/or polycarbonate (PC) [1]. In these compounds chlorine is attached to an aliphatic chain as well as to an aromatic ring. On the other hand the oils used as a feedstock for chemical industry should be free from chlorine compounds.

It is generally accepted that oils for universal use should not contain more than 10 ppm of Cl [5]. Efficiency of thermal dehydrochlorination (DHC) or hydrodechlorination (HDC) of organochlorines depends on the structure of these compounds [5—7]. DHC with metal oxides is more efficient than thermal DHC but leaves new harmful waste *i.e.* metal chlorides. Moreover, the purification is not always complete, while the required thermal DHC temperature is very high (400—500 °C) [8]. Optimal for the purification would be an adsorbent, which chemisorbs organochlorine compounds at lower temperatures than the temperature of the oil dehydrogenation, and which could be easily regenerated. We assumed that silver or platinum may be used as such sorbents. These

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metals, often used as catalysts, are chlorine sensitive at ppm levels of the chlorine compounds content in a reaction feed. It is important, that the contamination of the catalysts was reversible [9—11].

The experiments described in this paper verify the hypothesis, that these catalysts can be used also as good, reversible adsorbents for organochlorine compounds, which are components of pyrolytic oil obtained from plastic waste. Because the organochlorine molecules are too large to penetrate small pores in the adsorbent [1], impregnation of these pores with silver should be avoided. In order to optimise impregnation process a silver salt with a large anion (silver lactate) has been used.

For experiments benzyl chloride, 3-chlorotoluene, dichlorobenzene and methyl *p*-chlorobenzoate were chosen. Benzyl chloride represents compounds with a polar chlorine atom (due to its allylic position). The other tested compounds are all aromatics with chlorine attached to the aromatic ring. Dechlorination of these organochlorine substances is very difficult.

EXPERIMENTAL

Materials

Silver lactate was prepared using lactic acid supplied by Fluka AG and silver sulfate delivered by PPB POCh.

The pure support (γ-Al_2O_3) and the alumina supported platinum catalyst (Pt/Al_2O_3) were received from Katalizator Ltd. (Kraków).

Toluene, benzyl chloride, and methyl *p*-chlorobenzoate were obtained from POCh, Poland.

Oil T110 (based on naphthalene derivatives) was from Nynas Naphthenic AB.

Decalin, 1,2-dichlorobenzene and 3-chlorotoluene were obtained from Fluka AG.

Hydrogen was from Linde Gaz Poland, Ltd.

Methods

The silver-based adsorbent was prepared according to method reported in [12—14]. Finally the supported silver ions were reduced to metallic silver with hydrogen. The content of Ag in Ag/Al_2O_3 (20 wt. %) was determined from the weight loss upon reduction of its lactate.

The adsorption experiments were carried out in a three-neck flask equipped with a stirrer, a NiCr-NiAl thermocouple and a reflux condenser. The organochlorine compounds were dissolved in alkylated aromatic hydrocarbons (*e.g.*, toluene, alkylnaphthalene oil) and the mixture was kept in contact with the adsorbent (silver or platinum) at the desired temperature. Hydrogen was used for regeneration of the adsorbent. The experiments were carried out in a designed in our laboratory pulse microreactor made of acid resistant steel, equipped with a thermocouple and a heating jacket. After several cycles of adsorption/regeneration, the surface of silver was regenerated with air. Both regenerations (*i.e.* with hydrogen or with air) were performed at the temperature of *ca*. 350 °C.

The post experimental mixtures were analyzed by gas chromatography (GC Model 8610B, SRI Instruments using FID detector) and silica capillary column (RTX-1, 0.5 mm I.D. × 30 mm long) coated with bonded dimethylpolysiloxane phase (0.25 μm thick).

RESULTS AND DISCUSSION

The initial tests were carried out using Ag/Al_2O_3 at the temperatures 20, 50 and 100 °C. In these experiments benzyl chloride, 3-chlorotoluene and methyl *p*-chlorobenzoate were dissolved in toluene. All mixtures were analyzed at the start and after one hour of interaction with Ag/Al_2O_3. Results are shown in Table 1. Benzyl chloride was adsorbed completely at the temperatures 50 °C and above. The adsorption efficiency of 3-chlorotoluene and methyl *p*-chlorobenzoate was only 40 % and 70 %, respectively even at 100 °C, but it can be anticipated, that the adsorption will be more efficient at higher temperatures.

T a b l e 1. Effect of temperature on adsorption efficiency on silver of selected organochlorine compounds (solved in toluene) after one hour of contact

Organochlorine compound	Adsorption efficiency, %			Chlorine residue ppm
	20 °C	50 °C	100 °C	
Benzyl chloride	40	100	100	0
3-Chlorotoluene	10	38	40	108
Methyl *p*-chlorobenzoate	43	59	70	59

The next experiment was carried out at 150 °C. A mixture of Oil T110 and decalin (1:1 volume ratio) was applied as a solvent. Decalin was used to lower viscosity of the solution. Adsorption of 1,2-dichlorobenzene as a function of time was investigated. The results are shown in Figure 1. The initial content of dichlorobenzene was 0.0127 g in 88 g of the solvent. Within two hours of adsorption, the content of the solute dropped to 0.0042 g, which corresponds to 35 ppm of chlorine. Experiments at higher temperatures are under way.

The experiments have proved that silver is a good adsorbent for organochlorine compounds from liquid phase and outlined an adsorption conditions. Analogous experiments were conducted with Pt/Al_2O_3 as the adsorbent. The results however are not so interesting as those obtained for silver. The concentration of 1,2-dichlorobenzene dissolved in Oil T110 decreased from 2000 ppm to 480 ppm of Cl after 1 hour of contact with Pt/Al_2O_3.

The experiments carried out in a pulse reactor were aimed to answer the following question: "Could the sil-

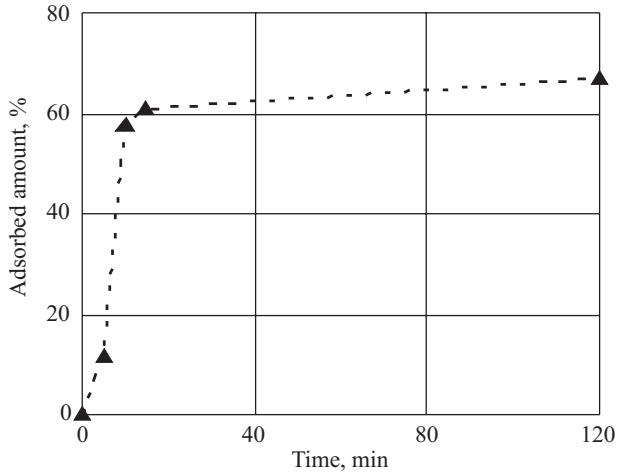

Fig. 1. Adsorption efficiency of 1,2-dichlorobenzene solved in mixture of Oil T110 and decalin (1:1 volume ratio) onto silver at temperature 150 °C as a function of time

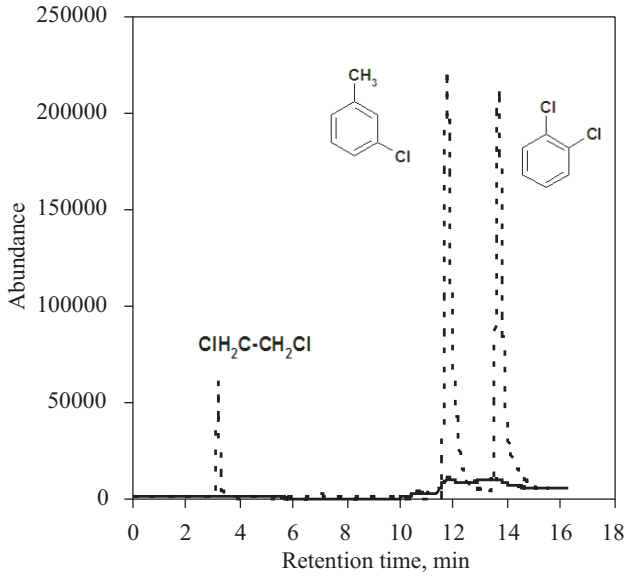

Fig. 2. Chromatograms of organochlorine compounds not adsorbed at temperature 200 °C in a microreactor filled with regenerated Ag/Al_2O_3 (solid line) and pure Al_2O_3 (dashed line)

ver surface be regenerated from chlorine?". Totally covered silver surface was treated with hydrogen at the temperature 300—350 °C and the regenerated silver was used again. The sample of organochlorine compounds solution was injected into the microreactor maintained at 200 °C, containing the regenerated adsorbent. Carrier gas passing through the microreactor was immediately directed into the chromatograph and analyzed. Presented in Figure 2 chromatogram shows that organochlorine compounds were almost completely adsorbed, which confirmed that silver has been successfully regenerated. Organochlorine content in the stream leaving the reactor dropped significantly (as in the experiment with freshly prepared adsorbent).

The presented results give affirmative answer to the posed question. Either silver or platinum can be used to remove organochlorine compounds from the pyrolytic oil without creating new, harmful inorganic waste (*i.e.* metal chlorides) and adsorption efficiency of silver is better then that of platinum. An advantage of this new method is low temperature of purification. The answer to the questions about maximal possible efficiency of the chlorine removal with silver or platinum adsorbents and about optimal conditions of the removal requires further studies. However, even if it turns out that the adsorption (chemisorption) efficiency of these metals is insufficient to reach the chlorine content in oil below 10 ppm, the proposed method is better and more attractive then chlorine removal with metal oxides.

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